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⑮ Cleaning using cyclodextrin.

⑮ A method of removing a surfactant from an environment containing the surfactant is provided, which comprises contacting the surfactant with an amount of cyclodextrin sufficient to bind all or part of the surfactant, thereby providing a cyclodextrin-bound surfactant, and separating the cyclodextrin-bound surfactant from the environment.

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## Description

## CLEANING USING CYCLODEXTRIN

The present invention relates to techniques for removing surfactants from various solutions and surfaces.

5 Surfactants, also known as detergents, are amphipathic compounds that have found wide use in removing dirt, oil, and the like from various surfaces. The resulting surface, however, is generally not free of contaminating surfactant compounds since there is a tendency for the surfactant molecules to stick to the surface being cleaned.

A number of agents have been proposed for removing detergent from surfaces being cleaned. These are generally known as rinsing agents and most often contain a non-ionic or an ionic surfactant. Such techniques, however, often just replace one surfactant with another. Other components of rinsing agent compositions, including starch degradation products such as dextrin, have been proposed for removing calcium ions from surfaces and for preventing calcium deposits. However, there remains a need for further development of rinsing agents capable of removing surfactants from surfaces.

10 Additionally, most rinsing agents have been provided as solutions for use in rinsing solid surfaces. In some cases, removal of surfactants from solution would be advantageous. Accordingly, development of solid-phase agents capable of removing surfactants from solutions is also desirable.

## SUMMARY OF THE INVENTION

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A method of removing surfactants from surfaces and from solutions is provided in which a cyclodextrin is contacted with an environment containing a surfactant, and the cyclodextrin-bound surfactant is then separated from the environment. The environment is typically an aqueous solution from which a surfactant is being removed or is a surface previously contacted (washed) with a surfactant. The cyclodextrin can be provided in either soluble or insoluble form. For example, an aqueous solution of a cyclodextrin is contacted with a previously washed surface in order to remove surfactant on that surface. The cyclodextrin is provided in an insoluble form for removing surfactants from solution or from surfaces, particles, or dissolved materials present or in contact with a solution.

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## DESCRIPTION OF SPECIFIC EMBODIMENTS

35 Cyclodextrins are cyclic amyloses. Three types are known: a cyclohexaamylose ( $\alpha$ -cyclodextrin), a cycloheptaamylose ( $\beta$ -cyclodextrin), and a cyclooctaamylose ( $\gamma$ -cyclodextrin). It was previously known that these cyclic amyloses form inclusion compounds (clathrates) and are capable of trapping a number of different organic molecules. However, the use of cyclodextrins to trap surfactants and remove them from a solution or from a surface was not known prior to this invention. Such use is unexpected in view of the amphipathic nature of surfactants.

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Cyclodextrins are well known compounds and are commercially available. For a description of their properties and methods of production, see, for example, Bender et al., *Cyclodextrin Chemistry*, Springer-Verlag, New York, 1978 (a 96-page book); French, *Adv. Carbohydr. Chem.* (1957) 12:189-260; Thoma et al., *Starch: Chemistry and Technology*, Vol. 1, Whistler et al., Eds., Academic Press, New York, 1965, pp. 209-249; and Cramer et al., *Naturwiss.* (1967) 154:625-635. The compounds are naturally occurring and are obtained from the action of *Bacillus macerans* amylase on starch.

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Cyclodextrins can be used to remove any detergent from a solution or solid surface. The mode of action is not certain, although it appears that at least a part of the detergent molecule is trapped into the interior space of the cyclodextrin. However, it is not clear whether all of the detergent molecule must be accommodated within the interior space. An exact fit does not appear to be necessary since different cyclodextrins will remove the same detergent from an environment.

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Although all three of the cyclodextrins are effective in removing surfactants, advantages are achieved by matching the size of the surfactant to the size of the interior space of the cyclodextrin. Large surfactants, such as those derived from cholic acid, are therefore most readily removed using  $\gamma$ -cyclodextrin, which has the largest interior space. Smaller surfactants, such as fatty acid salts and fatty sulfonates, are most readily removed with  $\alpha$ -cyclodextrin, which has the smallest interior space of the three cyclodextrins.

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Advantages are also achieved by providing a cyclodextrin in a form which can be readily separated from the environment from which a surfactant is being removed, preferably by a phase separation process (e.g., filtering). For example, soluble cyclodextrins dissolved in aqueous solutions are particularly suitable for use as rinsing solutions to remove surfactants from solid surfaces. Soluble cyclodextrins are less useful in removing surfactants from solutions as the cyclodextrin-surfactant inclusion complex tends to remain in solution.

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However, when a solution containing a soluble cyclodextrin is mixed with a solution from which surfactants are desirably being removed, the trapping and holding of surfactants by the cyclodextrins can be considered in

some sense to be a removal of the surfactant from the solution since the surfactant is not free to interact with the solution. For the purposes of this application, however, such an interaction will be considered to be a neutralization rather than a removal of the surfactant.

Accordingly, cyclodextrins attached to a solid surface, such as a polystyrene or latex bead, are more useful for actually removing surfactants from solution rather than neutralizing surfactant molecules in solution. Providing cyclodextrins attached to a solid particle or otherwise in a solid phase allows easy separation of phases by filtration or similar techniques. Numerous techniques have been developed for binding biological molecules, such as cyclodextrins, to solid surfaces, and any known or hereafter discovered techniques can be used. Such techniques generally involve formation of a covalent bond between a hydroxyl group of a cyclodextrin and either a reactive group on the surface of the solid or one end of a bifunctional molecule, the other end of which forms a covalent bond to the solid surface. Functional groups are typically present on the solid surface or the surface can be modified to contain functional groups capable of entering into covalent-bond-forming reactions. For example, amino and/or carboxy groups are present at the termini of polyamides. Hydroxyl groups are present in cellulosic materials. The benzene ring of polystyrene can be modified to contain functional groups such as hydroxyl or chloromethyl groups. Many organic surfaces can be oxidized to form carboxylate groups. Since the surfactant-removing capacity of cyclodextrins is insensitive to conformational changes, it is well within the skill of an ordinary chemist to covalently link a cyclodextrin to a functional group on a solid surface using a bifunctional reagent. Commercially available cyclodextrin polymers are also available. When formed into beads or other forms of suitable size, the polymeric cyclodextrin can be separated from solution by filtration.

The form of the solid to which a cyclodextrin is attached is not important to the practice of the present invention. However, microporous materials having cyclodextrins bound to the pore walls provide a greatly enhanced surface area on which binding can take place, since the actual surface of the solid will be significantly larger than its exterior gross surface.

Suspensions of solid-bound cyclodextrins will also typically be useful in removing surfactants from surfaces since contact of such an aqueous suspension with a surfactant-contaminated surface initially results in dissolution of some or all of the surfactant into the aqueous solution. The presence of a surface-bound cyclodextrin in such a suspension shifts the equilibrium of this dissolution reaction (provided sufficient cyclodextrin is present) until the surfactant has been essentially removed from the contaminated surfaces. It should be realized that the surface in question can be the surface of a biologically active molecule, such as an enzyme or other protein, in solution. Accordingly, what appears to be removal of a surfactant from solution by a solid-phase cyclodextrin may in fact be removal of a surfactant from the surface of biological molecules in solution. This nonetheless can easily result in a separation of phases since the relatively small soluble biological macromolecules can be separated by filtration from cyclodextrin bound to relatively large particles.

The use of any amount of cyclodextrin reduces the amount of surfactant on a surface being treated. Accordingly, use of any amount of cyclodextrin to remove surfactant falls within the scope of the broadest aspects of the present invention. However, it is preferred to use a molar excess of the cyclodextrin in order to remove trace amounts of the detergent without requiring excessive equilibrium times. Generally satisfactory rinse solutions can be prepared as aqueous solutions containing from .01% (w/v) cyclodextrin up to the solubility limit of the cyclodextrin being used. Different degrees of surfactant removal are achieved by varying the rinse procedure, with multiple rinses and larger amounts of rinsing agent being used to achieve the best removal of surfactants. When a solid-bound cyclodextrin is being used, the amount used can likewise vary over a wide range with satisfactory results. In order to increase the surface area available, it is preferred to provide the cyclodextrin bound to small particles or a porous surface in order to remove surfactants from solution. Columns of porous beads or the like can be easily prepared and used to remove cyclodextrins from solutions or from the surfaces of soluble molecules present in such solutions by passing the surfactant-containing solution through a column containing cyclodextrin.

A wide variety of surfactants can be removed from surfaces and solutions using cyclodextrins. Specific examples of suitable detergent compounds which can be removed in accordance with the present invention include the following:

Water-soluble soaps, such as the sodium, potassium, ammonium and alkanol-ammonium salts of higher fatty acids (C<sub>10</sub>-C<sub>22</sub>), and, particularly sodium and potassium tallow and coconut soaps.

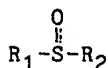
Anionic synthetic non-soap detergents, which can be represented by the water-soluble salts of organic sulfuric acid reaction products having in their molecular structure an alkyl radical containing from about 8 to 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Examples of these are the sodium or potassium alkyl sulfates, derived from tallow or coconut oil; sodium or potassium alkyl benzene sulfonates; sodium alkyl glyceryl ether sulfonates; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol and about 1 to 6 moles of ethylene oxide; sodium or potassium alkyl phenol ethylene oxide ether sulfonates, with 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide, sodium or potassium salts of fatty acid amide of a methyl tauride; and sodium and potassium salts of SO<sub>3</sub>-sulfonated C<sub>10</sub>-C<sub>24</sub>  $\alpha$ -olefins.

Nonionic synthetic detergents made by the condensation of alkylene oxide groups with an organic hydrophobic compound. Typical hydrophobic groups include condensatin products of porpylene oxide with

propylene glycol, alkyl phenols, condensation product of propylene oxide and ethylene diamine, aliphatic alcohols having 8 to 22 carbon atoms, and amides of fatty acids.

Also nonionic detergents such as amine oxides, phosphine oxides and sulfoxides having semipolar characteristics can be removed. Specific examples of long chain tertiary amine oxides include dimethyldodecylamine oxide and bis-(2-hydroxyethyl) dodecylamine. Specific examples of phosphine oxides are found in U.S. Patent No. 3,304,263 which issued February 14, 1967, and include dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl) phosphine oxide.

Removable long chain sulfoxides include those corresponding to the formula



wherein R<sub>1</sub> and R<sub>2</sub> are substituted or unsubstituted alkyl radicals, the former containing from about 10 to about 28 carbon atoms, whereas R<sub>2</sub> contains from 1 to 3 carbon atoms. Specific examples of these sulfoxides include dodecyl methyl sulfoxide and 3-hydroxy tridecyl methyl sulfoxide.

Examples of ampholytic synthetic detergents are sodium 3-dodecylaminopropionate and sodium 3-dodecylaminopropane sulfonate.

Examples of zwitterionic synthetic detergents include 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate.

Additionally, all of the following types of surfactants can be removed by the process of the present invention: (a) soaps (i.e., alkali salts) of fatty acids, rosin acids, and tall oil; (b) alkyl arene sulfonates; (c) alkyl sulfates, including surfactants with both branched-chain and straight-chain hydrophobic groups, as well as primary and secondary sulfate groups; (d) sulfates and sulfonates containing an intermediate linkage between the hydrophobic and hydrophilic groups, such as the fatty acylated methyl taurides and the sulfated fatty monoglycerides; (e) long-chain acid esters of polyethylene glycol, especially the tall oil esters; (f) polyethylene glycol ethers of alkylphenols; (g) polyethylene glycol ethers of long-chain alcohols and mercaptans; (h) fatty acyl diethanol amides; and (i) block copolymers of ethylene oxide and propylene oxide. Since surfactants can be classified in more than one manner, a number of classes of surfactants set forth in this paragraph overlap with previously described surfactant classes.

A particularly useful application of the present invention is in clearing solutions and container surfaces used in biochemical reactions of surfactants. Since surfactants tend to disrupt the three-dimensional shape of macromolecules, such as proteins, assays which rely on binding interactions between macromolecules and/or enzymes to produce detectable signals are often disrupted by trace amounts of surfactants used to clean reagent containers, whether during routine cleaning of laboratory glassware or during rinse steps of various assay procedures. Sensitivity can therefore be enhanced by removing surfactants from the surfaces and solutions that contact the biochemical components of such assays.

In this regard, there are a number of detergents specifically designed for and commonly used in biological situations. For example, a number of biological detergents (surfactants) are listed as such by Sigma Chemical Company on pages 310-316 of its 1987 Catalog of Biochemical and Organic Compounds. Such surfactants are divided into four basic types: anionic, cationic, zwitterionic, and nonionic. Examples of anionic detergents include alginic acid, caprylic acid, cholic acid, 1-decanesulfonic acid, deoxycholic acid, 1-dodecanesulfonic acid, N-lauroylsarcosine, and taurocholic acid. Cationic detergents include dodecyltrimethylammonium bromide, benzalkonium chloride, benzyltrimethylhexadecyl ammonium chloride, cetylpyridinium chloride, methylbenzethonium chloride, and 4-picoline dodecyl sulfate. Examples of zwitterionic detergents include 3-[(3-cholamidopropyl)-dimethylammonio]-1-propanesulfonate (commonly abbreviated CHAPS), 3-[(cholamidopropyl)-dimethylammonio]-2-hydroxy-1-propanesulfonate (generally abbreviated CHAPSO), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate, and lyso-α-phosphatidylcholine. Examples of nonionic detergents include decanoyl-N-methylglucamide, diethylene glycol monopentyl ether, n-dodecyl β-D-glucopyranoside, ethylene oxide condensates of fatty alcohols (e.g., sold under the trade name Lubrol), polyoxyethylene ethers of fatty acids (particularly C<sub>12</sub>-C<sub>20</sub> fatty acids), polyoxyethylene sorbitan fatty acid ethers (e.g., sold under the trade name Tween), and sorbitan fatty acid ethers (e.g., sold under the trade name Span). Mixtures of these and other surfactants can also be removed by cyclodextrins.

The use of the detergents per se is not a part of the present invention. Rather, the present invention comes into play after the detergents are used. Cyclodextrins are used to remove the detergent (surfactant) from the surface on which or the solution in which the detergent is present. Examples of surfaces are cloth, metal, painted and waxed surfaces, glass, plastic and the like. For example, cyclodextrins can be used in the rinse cycle of automatic clothes washers, dishwashers and labware washers. Cyclodextrins can also be used to remove detergents from building and/or automobile surfaces (such as after washing and prior to painting or waxing).

The invention now being generally described, the same will be better understood by reference to the following examples which are provided for purposes of illustration only and are not intended to be limiting of the invention unless so specified.

EXAMPLE

Various amounts of unswollen, unwashed  $\beta$ -cyclodextrin polymer (BCP) were incubated for 24 or 72 hours with aqueous solutions of lithium dodecylsulfate (LIDS) at room temperature to determine if BCP could remove LIDS from solution. The ratios of LIDS to BCP ranged from 0.25  $\mu\text{g}/\text{mg}$  to 20  $\mu\text{g}/\text{mg}$ . Assuming that all of the cyclodextrin monomers were functional and accessible to the LIDS, the latter figure would represent a molar ratio of approximately 1:12 (LIDS to BCP).

LIDS concentration in solution (and thus the ability of BCP to remove LIDS from solution) was determined by measuring the activity present in an enzyme acceptor-enzyme donor complementation assay. This assay is summarized below and is described in detail in U.S. Patent Application Serial No. , filed April 6, 1987 by Khanna et al. entitled "Reagent Stabilization in Enzyme-Donor Acceptor Assay." This complementation assay is based on the ability of fragments of  $\beta$ -galactosidase to reassemble. The smaller fragment is referred to as the enzyme donor and the larger fragment as the enzyme acceptor. When both fragments are present in solution they reassemble to form an active enzyme. This complementation is inhibited by LIDS. Standard solutions of as little as 0.015% LIDS were shown to completely inhibit the complementation reaction.

Assay conditions were as follows: 25  $\mu\text{L}$  of 13 nM ED4-T4 (enzyme donor attached to a T4 ligand) in assay buffer (150 mM potassium phosphate, 100 mM sodium phosphate, 10 mM EGTA (ethylene glycol tetraacetic acid), 2 mM magnesium acetate, 20 mM sodium azide, 0.05% Tween-20, 0.05 mM DTT (dithiothreitol), and 2.4% ethylene glycol, pH 7.0), and 100  $\mu\text{L}$  of 2.19 mg/ml CPRG (chlorophenol red  $\beta$ -D-galactopyranoside, a  $\beta$ -galactosidase substrate) in assay buffer were mixed in the lower well of a Baker Encore sample disk. The upper well contains 25  $\mu\text{L}$  of 5,000 nM EA (enzyme acceptor) in assay buffer with 100  $\mu\text{L}$  of either a LIDS standard solution (w/v%) or the liquid component of the BCP/LIDS incubation. The reaction was performed on the Baker Encore instrument at 37°C.

The result of varying the concentration of LIDS and the ratio of LIDS to BCP are shown in the following tables. Table 1 shows the enzyme activity after complementation in solutions (as described above) which contained the indicated concentrations of LIDS. These data show the effects of surfactant on enzyme complementation.

Table 1  
72 Hour Incubation: Effect of  
Surfactant in Absence of Cyclodextrin

<u>% LIDS</u>	<u>Complementation</u> <u>Activity (mA/sec)</u>
0	7.4
0.005	4.5
0.01	0.9

A concentration of 0.005% LIDS produced a complementation activity only about 60% that of a standard solution not containing any LIDS. For a concentration of 0.01% LIDS, the corresponding complementation activity was only about 10% of the normal activity.

In contrast, when LIDS in the concentration range of 0.004 to 0.033% (w/v) was incubated for 72 hours with BCP in the ratios set forth in Table 2 below, complementation activities were very similar to those for standard solutions not containing any LIDS. This experiment demonstrates that the cyclodextrin polymer is capable of removing essentially all of the added LIDS from solution.

Table 2

72 Hour Incubation: Effect of  
Surfactant in Presence of Cyclodextrin

<u>ug LiDS/mg BCP</u>	<u>Complementation</u> <u>Activity (mA/sec)</u>
0.25	7.6
0.5	7.6
1.0	8.2, 7.8
2.0	7.4, 6.8
4.0	7.8

Similar experiments were carried out for a 24-hour incubation. Complementation activity for assay solutions containing different concentrations of LIDS are set forth in Table 3.

Table 3

24 Hour Incubation: Effect of  
Surfactant in Absence of Cyclodextrin

<u>% LiDS</u>	<u>Complementation</u> <u>Activity (mA/sec)</u>
0	4.8
0.005	3.7
0.01	0.5
0.025	0.03

Results for 24-hour incubations for varying amounts of LIDS and ratios of LIDS to BCP are set forth in Table 4.

Table 4

24 Hour Incubation: Effect of  
Surfactant in Presence of Cyclodextrin

<u>ug LiDS/mg BCP</u>	<u>% LiDS</u> <u>Solution</u>	<u>Complementation</u> <u>Activity (mA/sec)</u>
--	0	5.3
1	0.014	5.1
2.5	0.036	4.9
5	0.071	5.2
10	0.143	5.1
20	0.286	4.1

When LIDS solutions containing the same concentrations of LIDS as set forth in Table 4 were incubated for 24 hours without BCP, activities of less than 0.04 mA/sec were obtained for all samples containing LIDS. However, when BCP was present, as indicated in Table 4, all complementation activities were similar to that

which was present in a solution not containing LIDS.

These data support the conclusion that a  $\beta$ -cyclodextrin polymer is capable of absorbing and sequestering a detergent, such as LIDS, from an aqueous solution. Potentially inhibitory concentrations of LIDS were incubated with the  $\beta$ -cyclodextrin polymer and assayed in a sensitive complementation assay. Complementation was not affected at any of the ratios of LIDS to BCP tested, thereby indicating that the BCP was preventing LIDS from affecting the complementation reaction. Controls indicated that soluble  $\beta$ -cyclodextrins were not released from the polymer, thereby eliminating this possibility as a cause of the indicated result.

All publications and patent applications mentioned in this specification are indicative of the level of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

The invention now being fully described, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto.

## Claims

1. A method of removing a surfactant from an environment containing said surfactant, which comprises:  
contacting said surfactant with an amount of a cyclodextrin sufficient to bind all or part of said surfactant, thereby providing a cyclodextrin-bound surfactant, and separating said cyclodextrin-bound surfactant from said environment.
2. The method of Claim 1, wherein said cyclodextrin is  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin,  $\gamma$ -cyclodextrin, or a cyclodextrin polymer.
3. The method of Claim 1, wherein said environment is an aqueous solution or suspension containing said surfactant and said cyclodextrin is bound to a solid phase.
4. The method of Claim 1, wherein said environment is a surface of a solid.
5. The method of Claim 1, wherein said environment is an aqueous solution containing a protein.
6. The method of Claim 1, wherein said surfactant is a water-soluble soap, anionic synthetic non-soap detergent, or non-ionic synthetic detergent.
7. The method of Claim 6, wherein said surfactant is a sodium, potassium, ammonium, or  $C_{10}$ - $C_{24}$  alkanol-ammonium salt of a  $C_{10}$ - $C_{22}$  fatty acid.
8. The method of Claim 6, wherein said surfactant is a water-soluble salt of an organic sulfuric acid reaction product containing a  $C_8$ - $C_{22}$  alkyl radical and a sulfonic acid or sulfuric acid ester radical.
9. The method of Claim 8, wherein said surfactant is a sodium or potassium alkyl sulfate, a sodium or potassium alkyl benzene sulfonate, a sodium or potassium fatty acid monoglyceride sulfate or sulfonate, a sodium or potassium salt of a sulfuric acid ester of a reaction product of one mole of a fatty alcohol and 1 to 6 moles of ethylene oxide, a sodium or potassium  $C_8$ - $C_{12}$  alkyl phenol ethylene oxide ether sulfonate containing 1 to 10 units of ethylene oxide per molecule, a reaction product of a fatty acid esterified with isethionic acid and neutralized with sodium hydroxide, a sodium or potassium salt of a fatty acid amide of a methyl tauride, a sodium or potassium salt of an  $SO_3$ -sulfonated  $C_{10}$ - $C_{24}$  alpha-olefin, or a mixture thereof.
10. The method of Claim 6, wherein said surfactant is a condensation product of a  $C_2$ - $C_3$  alkylene oxide with an organic hydrophobic compound.
11. The method of Claim 1, wherein said separating comprises providing said cyclodextrin in a solid or aqueous phase different from the phase of said environment and carrying out a phase separation reaction.



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6944

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y,A	CHEMICAL ABSTRACTS volume 98, no. 04, 1983, Columbus, Ohio, US, page 372, column 1, abstract no. 22675z; K. KRALOVA et al.: "Interactions of alpha-cyclodextrin with ionic detergents"; & PROC. INT. SYMP. CYCLODEXTRINS, 1st 1981 ---	1,2	C 11 D 3/00 C 11 D 3/22
Y,A	CHEMICAL ABSTRACTS volume 106, no. 03, January 1987, Columbus, Ohio, USA, page 645, column 2, abstract no. 18963h; A. HERSEY et al.: "Mechanism of inclusion compound formation for binding of organic dyes, ions, and surfactants to alpha-cyclodextrin studied by kinetic methods based on competition experiments"; & J. CHEM. SOC., FARADAY TRANS. 1, 1986, 82(5) ---	1,2,6,9	
P,A	CHEMICAL ABSTRACTS volume 108, no. 24, June 1988, Columbus, Ohio, USA, page 118, column 1, abstract no. 206695n; W. SAENGER et al.: "Cyclodextrins increase the surface tension and the critical micelle concentration of detergent solutions"; & ANGEW. CHEM. 1988, 100(3) --- -/-	1,2,6, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)  C 11 D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 20-10-1988	Examiner PELLE WABLATB
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document			

EPO FORM 153 (3.82) (P6401)





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Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS volume 103, no. 26, 1985, Columbus, Ohio, USA, page 397, column 1, abstract no. 221391a; I. SATAKE et al.: "Conductometric and potentiometric studies of the association of alpha-cyclodextrin with ionic surfactants and their homologs"; & BULL. CHEM. SOC. JPN. 1985, 58(10) ----	1,2,6,9	
A	CHEMICAL ABSTRACTS volume 105, no. 22, 1986, Columbus, Ohio, USA, page 354, column 2, abstract no. 196641p; M. KIMURA et al.: "Selective adsorption of components in dyeing wastewater by a cellulosic adsorbent and reuse of the treated wastewater"; & MIZU SHORI GIJUTSU 1986, 27(7) ----	1-3,6	
A	GB-A-1 069 358 (BOEHME FETTCHEMIE GMBH) * page 2, lines 2-4; claims * -----	1,6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 20-10-1988	Examiner PELLE WABLATB
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

EPO FORM 150 (3.82) (P0601)